CONSOLIDATION OF POLYCRYSTALLINE YTTRIA POWDER BY MIL-LIMETER-WAVE SINTERING FOR LASER HOST APPLICATIONS*

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Abstract

We report recent results of an investigation of millimeter-wave processing of yttria (Y_2O_3) for fabrication of transparent, high strength polycrystalline ceramic laser hosts for High Energy Laser (HEL) applications.[1,2] The objective is to produce polycrystalline materials with optical quality comparable to that of a single crystal. It is difficult to produce yttria single crystals because of the phase transformation around 2000°C and the high melting temperature which is over 2400°C. While single crystals have high thermal conductivity and can operate at high powers, they are costly and limited in size and dopant concentration. Significant advantages of polycrystalline materials compared to single crystals, are lower processing temperature, higher gain as a result of higher dopant concentrations, faster and less expensive fabrication, and the possibility of larger devices. Millimeter-wave processing has been proposed as an alternative method to solve the problems of both conventional vacuum sintering and low frequency microwave sintering, such as low heating rates, poor coupling, and unfavorable thermal gradients. A major component of the NRL millimeter-wave processing facility is a 20-kW, continuous-wave (CW), 83-GHz gyrotron oscillator (GYCOM, Ltd.). Translucent yttria has been successfully sintered with millimeter-wave beams with up to 99% theoretical density. A partially transparent yttria ceramic sample has also been achieved using the millimeter-wave sintering process. Several factors impact the quality of the sintered material including the presence of agglomerates, impurities, processing atmosphere, sintering aids, and thermal gradients. Efforts to improve the transparency are in progress.

I. INTRODUCTION

Single crystal Nd-doped YAG has been the most widely used solid-state laser material [2]. Current materials for solid-state lasers include single crystals of neodymium-doped YAG and neodymium glasses. While single crystals have high thermal conductivity and can operate at high powers, they are costly and limited in size and dopant concentration. Neodymium-containing glasses can be large with reasonable cost but have low thermal conductivity, thereby limiting average power. Recently, polycrystalline Nd-doped YAG with excellent lasing properties has become available, and the potential of Yb-doped Y_2O_3 was demonstrated as a novel diode-pumped laser host [3]. Significant advantages of transparent polycrystalline laser host materials for high energy laser (HEL) applications, compared to single-crystal materials, are reduced processing temperatures, greatly reduced processing times, elimination of facet and core structures, and the possibility of higher dopant concentrations. In addition, polycrystalline laser host materials have good thermal conductivity, high mechanical strength, and, in principle, can be fabricated into large and complex structures. However, the powder preparation and the sintering conditions must be carefully controlled in order to realize these advantages.

Millimeter-wave processing has been shown to be an effective alternative to conventional vacuum furnaces for pressure-free sintering of low-loss oxide ceramic materials [4]. The driving force for this type of sintering is the excess surface energy of the grains. For ceramics this is $\gamma \sim 1$ J/m^2 and the resulting stress is: $\sigma^s \sim 2\gamma/R \sim 4$ MPa for R=0.5 µm. Mass transport occurs via lattice vacancy diffusion along grain boundaries at $T \sim 0.5$–0.75 of the melting point temperature. Vacancy diffusion proceeds by a jump process; near equilibrium $D_v = D_{v0}e^{-Q_v/k_BT}$ where D_v is the diffusion coefficient and Q_v is the activation energy barrier for the vacancy to exchange position with a lattice ion. Vacancy diffusion is also an important microwave coupling mechanism in oxide ceramics so one expects that the microwave heating and sintering processes will be closely related. In fact, microwave sintering often results in superior microstructure with fewer trapped pores, cleaner grain boundaries, and smaller grain size than conventionally sintered materials. These properties are critical to achieving high optical quality, transparent laser host materials. Other advantages of microwave processing include faster heating rates and the capability to sinter at lower temperatures than conventional heating, resulting in a shorter more efficient process [5].

A critical feature of millimeter-wave sintering is stronger coupling to laser host materials than conventional microwaves. Sesquioxides have very low rf loss and do not couple well at low frequencies (*e.g.* 2.45 GHz) compared to high frequencies (*e.g.* 83 GHz). The absorbed

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14. ABSTRACT
We report recent results of an investigation of millimeter- wave processing of yttria (Y2O3) for fabrication of transparent, high strength polycrystalline ceramic laser hosts for High Energy Laser (HEL) applications.1,2 The objective is to produce polycrystalline materials with optical quality comparable to that of a single crystal. It is difficult to produce yttria single crystals because of the phase transformation around 2000°C and the high melting temperature which is over 2400°C. While single crystals have high thermal conductivity and can operate at high powers, they are costly and limited in size and dopant concentration. Significant advantages of polycrystalline materials compared to single crystals, are lower processing temperature, higher gain as a result of higher dopant concentrations, faster and less expensive fabrication, and the possibility of larger devices. Millimeter-wave processing has been proposed as an alternative method to solve the problems of both conventional vacuum sintering and low frequency microwave sintering, such as low heating rates, poor coupling, and unfavorable thermal gradients. A major component of the NRL millimeter-wave processing facility is a 20-kW, continuous-wave (CW), 83-GHz gyrotron oscillator (GYCOM, Ltd.). Translucent yttria has been successfully sintered with millimeter-wave beams with up to 99% theoretical density. A partially transparent yttria ceramic sample has also been achieved using the millimeter-wave sintering process. Several factors impact the quality of the sintered material including the presence of agglomerates, impurities, processing atmosphere, sintering aids, and thermal gradients. Efforts to improve the transparency are in progress.

15. SUBJECT TERMS

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power per unit volume in a ceramic is proportional to the microwave frequency, ω, and loss according to

$$P_{absorbed}(\omega,T) = \frac{1}{2}\omega\varepsilon_0\varepsilon''(\omega,T)|E|^2 \quad [6]$$

where ε_0 is the free space permittivity, ε'' is the relative dielectric loss and E is the local rf field. Thus the power loss is a function of both the temperature T of the ceramic and the frequency; at a given frequency, oxide ceramics tend to be more absorbing at higher temperatures, and at a given temperature, an oxide ceramic is more absorbing at higher frequencies. These effects are illustrated in Fig. 1, which shows the temperature rise of an insulated semi-infinite yttria slab heated for one minute by a 100 W/cm^2 normally incident microwave beam. The frequency dependence of the power absorption is an important motivation for processing low-loss ceramics at 83 GHz rather than at 2.45 GHz or 35 GHz. However, the strong coupling reduces the penetration distance of the fields limiting workpiece size. This effect is illustrated in Fig. 1(b).
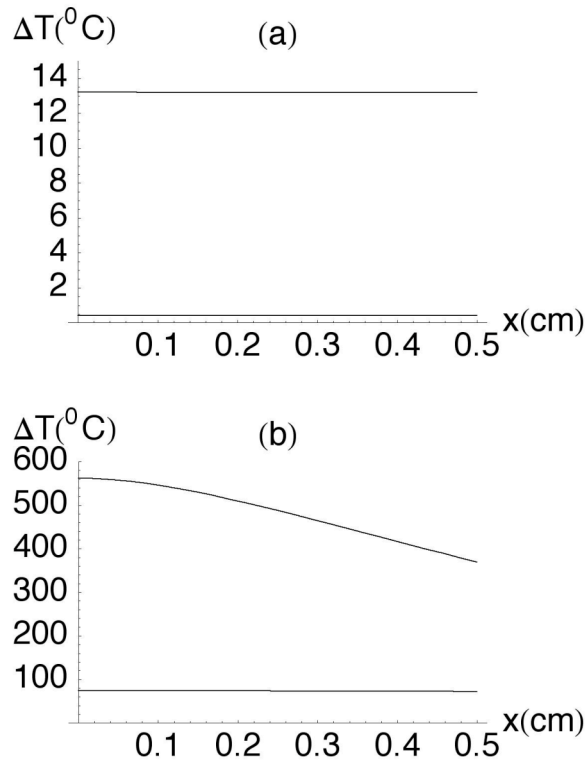

Figure 1. Heating of an insulated semi-infinite yttria slab by a 100 W/cm^2 plane-wave microwave beam for one minute. Upper curves correspond to 83 GHz and lower curves to 2.45 GHz. (a) initial temperature is 20°C, (b) initial temperature is 1500 °C.

Green powder and processing issues are important in producing transparent ceramics. The purity of raw materials is very critical in laser materials relative to the electronic state of dopants. A homogeneous distribution of dopants in the final product and dopants incorporated into crystal structure of host material is important. The powders must be capable of being compacted into preforms of uniformly high green density (larger than 50–60% of the theoretical density). The powders must sinter readily without exaggerated or anomalous grain growth (*i.e.* large grains growing at the expense of small grains). Normally, this may require use of small quantities of sintering aids; however, sintering aids can degrade optical transparency. The raw materials must be clean or be cleaned prior to sintering to remove adsorbed species, binders, and surface contaminants (water, hydroxides, carbonates, organics) to provide for good sinterability. Thermal treatments required may include low temperature heat treatment to remove adsorbed gases and surface contaminants, intermediate temperature heat treatment to homogenize phase structure and chemistry and high temperature heat treatment for sintering to near theoretical density.

II. SINTERING EXPERIMENTS

A. Equipment

The NRL gyrotron-based material processing facility (*cf.* Fig. 1) features a 20 kW, CW, 83 GHz GYCOM gyrotron oscillator, which can generate between 1 W/cm^2 – 2 kW/cm^2 irradiance. The facility features a quasi-optical beam system for beam focusing and manipulation and an inner vacuum chamber (30,000 cm^3) for precise atmosphere control and vacuum processing to 10^{-3} Torr. The gyrotron is operated via a fully automated computerized control system written in the LabVIEW™ platform with feedback from extensive in-situ instrumentation and visual process monitoring. The system has the capability of sample rotation and translation during processing.
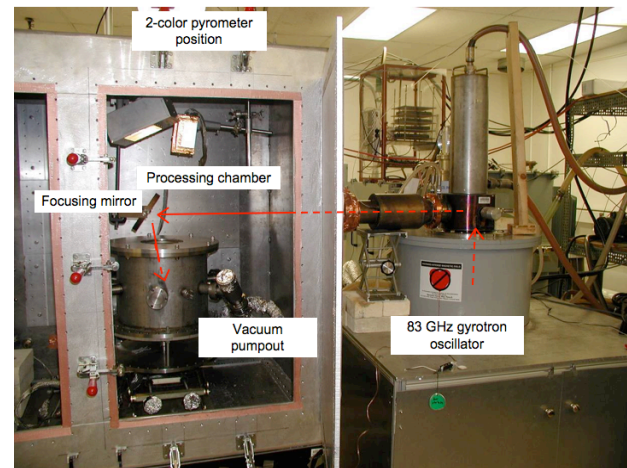

Figure 2. Photograph of the NRL 83 GHz millimeter-wave materials processing facility.

B. Processing set-up

The ceramic work pieces were processed in a vacuum of approximately 50 milliTorr. A small vacuum chamber (inner diameter 33 cm, height 28 cm) (*cf.* Fig. 2) is used for millimeter-wave processing. The temperature is monitored by both an S-type thermocouple (platinum/platinum with 10% rhodium) situated near the sam-

ple and a remotely located optical two-color pyrometer which reads the temperature through an 83-GHz, tuned, quartz window above the sample. The ceramic work piece is embedded in a setter powder and/or microwave susceptor. Zirconia was often used as a setter powder and other setter powders include boron nitride, alumina, and yttria. The sample is often placed inside a small boron nitride crucible as shown in Fig. 3 to both protect it from contamination and provide a more uniform thermal bath. All samples were uniaxially pressed, with green densities ranging between 50 and 60% of theoretical density (TD).
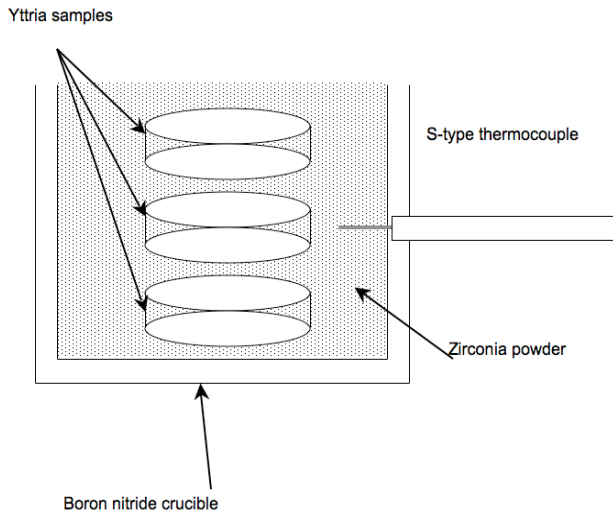

Figure 3. Small open casket used for sintering 6 mm diameter compacts

The automated temperature controller elevates the sample temperature using feedback from the thermocouple and two-color pyrometer (by increasing the gyrotron voltage and consequently its output power) at a predetermined rate of approximately 20°C per minute until it reaches a maximum temperature of 400–500°C, where it is maintained for 0.5 hour. This phase serves two purposes: it allows moisture, organics, adsorbed gases, and chemisorbed species to fully escape at the grain boundaries to provide high optical quality [7] and also allows the ceramic to couple more efficiently to the millimeter-wave beam as discussed above. The sintering process is completed by raising the sample to high temperature, between 1600 and 1700°C, where it is maintained via thermal feedback for up to one hour. A much higher heating rate is possible with the millimeter-wave beam compared to conventional heating; however a lower heating rate is usually chosen, using the monitored pressure as a metric, to allow for escape of volatiles to minimize trapped pore formation. Sintering occurs during a 30–60 minute hold at peak temperature of between 1600 and 1700°C. Two side-by-side samples can be processed simultaneously in a beam having an elliptical cross section with an area of about 4 cm^2. The permitted cooling rate is limited by thermal stresses in the component and surrounding materials. A typical temperature profile is shown in Fig. 4.

Low temperatures (< 700^{0}C) are monitored using the S-type thermocouple, which is also used to control the low temperature heating rate. At high temperatures the temperature measured by the pyrometer, which looks at the work piece surface, is considered more representative of the work piece temperature and is used for computer control. Note that the agreement between the pyrometer and thermocouple readings improves during the run as the thermal system approaches equilibrium.

C. Yttria

The yttria powder used in our studies was purchased from Inframat and was stated to be of submicron size. We also used Yb-doped (2% weight concentration) Yttria powder produced at NRL from chloride precursors and provided by J. Sanghera (private communication). Samples were sintered uniformly to almost theoretical density (96%) starting with uniaxially pressed (UP) yttria powder to 54-57% TD. In this case, three 140-mg 6-mm-diameter Inframat samples were stacked and embedded in fine zirconia powder inside a boron nitride crucible as indicated in Fig. 3. The samples were sintered by raising the temperature 20°C per minute and holding it at 1600°C for 60 minutes. After the experiment, the samples were polished and the center sample was found to have a density that was 96% TD (Table I, column 1), while the top and bottom samples had slightly lower density (94% TD). Table I shows the green and sintered densities of representative samples used in these experiments. Some of the samples were cold isostatically pressed (CIP) at 45 kpsi to increase the green density. However, cold isostatically pressing the Inframat samples after uniaxially pressing did not significantly improve the sintered result (94.5%TD vs. 96.0%TD). The Inframat powder sintered to higher densities than the Sanghera powder, probably due to the presence of hard agglomerates in the latter powder. According to optical microscopy, in all cases the green samples have 3-10 micron grain size whereas the sintered samples have 20-60 micron grain size (*cf*. Fig. 5). The relatively large size of the green powder indicates the presence of agglomerates. These may account for the larger than expected final grain sizes.
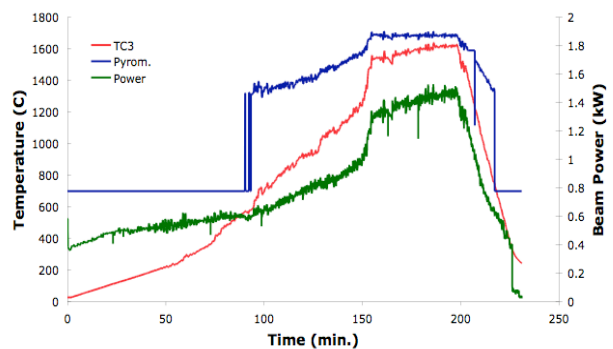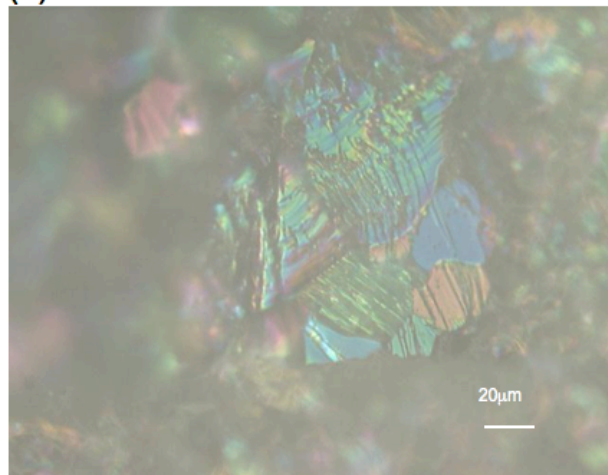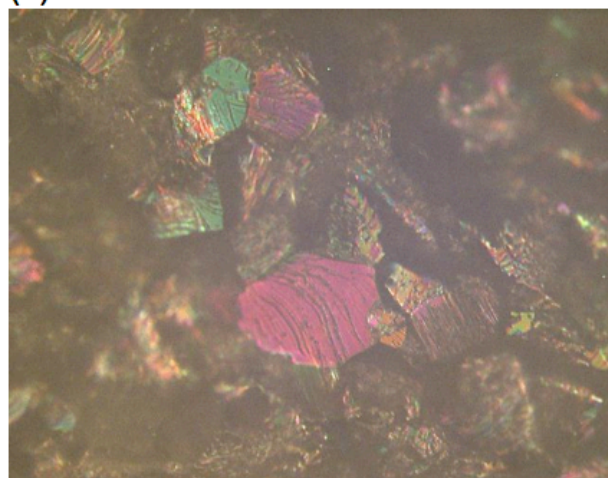

Figure 4. Temperature and power profiles for Inframat sample (see Table I, Col. 1) sintering run.

Table I. Yttria density and grain size measurements.

Powder source	Inframat	Inframat	NRL
Material	Y_2O_3	Y_2O_3	$Yb:Y_2O_3$
CIP?	No	Yes	Yes
Green %TD	56.8	60.8	58.8
Mass (mg)	145	144	136
Diameter (mm)	5.06	5.08	5.17
Thickness (mm)	1.50	1.50	1.41
Sintered %TD	96.0	94.5	89.7
Grain size (μm)	20-60	20-60	20-60

(a)

(b)

Figure 5. Optical micrographs showing grain size of sintered samples. (a) Inframat Yttria powder, (b) NRL Yb(2wt%):Y_2O_3 powder.

III. CONCLUSION

Millimeter-waves can be applied to the sintering of polycrystalline ceramic laser materials. Millimeter-wave sintering decreases processing time compared to conventional methods and allows more flexibility in choosing the thermal profile. Most densification occurs within the first 30 minutes at peak temperature. Our best results are obtained with samples in protective boron nitride crucibles, surrounded by a lossy setter powder providing thermal insulation and acting as a susceptor. Yttria has been sintered to near theoretical density with uniform shrinkage and good grain structure. Transparency may require improved (un-agglomerated, higher purity) powder, higher green density, calcining, or a final hot isostatic pressing (HIP) step.

IV. ACKNOWLEDGMENTS

V. REFERENCES

[1] M. Lombardi, A. W. Fliflet, *et al.*, "Millimeter-wave sintering of polycrystalline ceramic laser materials", IRMMW-THz 2005, (2005).

[2] A. Ikesue and I. Furusato, "Fabrication of polycrystalline, transparent YAG ceramics by a solid-state reaction method", J. Am. Ceram. Soc., **78** 225-28 (1995).

[3] J. Kong, D. Y. Tang, B. Zhao, J. Lu, K. Ueda, H. Yagi and T. Yanagitani, "9.2-W diode–end–pumped Yb:Y_2O_3 ceramic laser," Appl. Phys. Lett. **86**, 161116 (2005).

[4] D. Lewis, M. A. Imam, *et al.*, "Material processing with a high frequency millimeter-wave source", Mat. Manuf. Proc. **18,** 151-167 (2003).

[5] R.W. Bruce, *et al.*, "Joining of ceramic tubes using a high-power 83-GHz Millimeter-wave beam", IEEE Trans. Plasma Sci. **33**, 668-678, 2005.

[6] K. G. Ayappa, H. T. Davis, E. A. Davis, and J. Gordon, "Analysis of Microwave Heating of Materials with Temperature-Dependent Properties", AIChE Journal **37**, 313-322, 1991.

[7] A. Ikesue and K. Yoshida, "Influence of pore volume on laser performance of Nd: YAG ceramics", J. Mat. Sci. **34**, 1189-1195, 1999.